

A quantum statistical mechanics model of a three dimensional linear rigid rotator in a bath of oscillators: IV- steady state dielectric properties induced by a.c and d.c field coupling.

J. T. Titantah[†] and M. N. Hounkonnou

Unité de Recherche en Physique Théorique,
Institut de Mathématiques et de Sciences Physiques,

B.P.: 613 Porto-Novo - Republic of Benin.

Abstract

The long time effect of a radio frequency (rf) a.c. field superimposed on a d.c. field on the electrical susceptibility and the Kerr optical functions of polarisable fluids in inert solvent is analysed. The results obtained for the classical Brownian limit, valid for dense solvent media, well reproduce classical results published in the literature with excellent precisions in inertia, density and temperature dependences. The low density limit yields absorption-dispersion lines whose widths and shifts are density, inertia and temperature dependent. While the low density and/or large inertia susceptibility is explicitly written out as a continued fraction got by solving an infinite hierarchy of differential coupled equations, that of the Kerr effect is given in the form of successive convergents of the solutions of an infinite hierarchy of differential difference triplets. The polarisation/a.c. field phase difference is analysed. The effects of the constant field strength and the a.c. field frequency on the Kerr function are explored. In this paper, which will be named paper IV, the derivation of some quoted equations will intensionally be left out as they exist in paper III (*J. Phys. A*, 30:6347, 1997) of which this work is its logical continuation.

[†]Present adress: *Département de Physique, Université Libre de Bruxelles, Brussels (Belgium)*

1 Introduction

In recent works [1, 2, 3], we derived a master equation describing the evolution of a system of linear rigid rotators in a bath of non interacting harmonic oscillators. Due to the fact that experimentally observed spectra are accounted for, strongly, by molecular rotational motions, we consider the rotational degrees of freedom of the rotator by defining an orientation operator $\hat{\mathbf{u}} = \hat{\mu}/\mu$, where $\hat{\mu}$ is the rotator permanent dipole moment of magnitude μ . The master equation for the statistical orientation probability density operator $\hat{\rho}_S(t)$ associated with the motion of the rotator in interaction with the bath and an external driving field is [1, 2]

$$\frac{\partial \hat{\rho}_S(t)}{\partial t} + \frac{i}{\hbar} [\hat{H}_S, \hat{\rho}_S(t)] + \hat{K} \hat{\rho}_S(t) = -\frac{i}{\hbar} [\hat{H}_E, \hat{\rho}_S(t)], \quad (1)$$

where \hat{H}_S is the rotator rotational kinetic energy operator, whose eigen-values are $E_l = (\hbar^2/2I)l(l+1)$ with $l = 0, 1, 2, \dots$

The collision term is written as

$$\begin{aligned} \hat{K} \hat{\rho}_S(t) = & \frac{\zeta}{I} \sum_{l=1}^{\infty} l \{ A_l^* \hat{\mathbf{u}} \cdot \hat{\mathbf{u}}_l^- \hat{\rho}_S(t) - A_l \hat{\mathbf{u}} \cdot \hat{\rho}_S(t) \hat{\mathbf{u}}_l^+ + B_l \hat{\mathbf{u}} \cdot \hat{\mathbf{u}}_l^+ \hat{\rho}_S(t) - B_l^* \hat{\mathbf{u}} \cdot \hat{\rho}_S(t) \hat{\mathbf{u}}_l^- \\ & - A_l^* \hat{\mathbf{u}}_l^- \cdot \hat{\rho}_S(t) \hat{\mathbf{u}} + A_l \hat{\rho}_S(t) \hat{\mathbf{u}}_l^+ \cdot \hat{\mathbf{u}} + B_l^* \hat{\rho}_S(t) \hat{\mathbf{u}}_l^- \cdot \hat{\mathbf{u}} - B_l \hat{\mathbf{u}}_l^+ \hat{\rho}_S(t) \cdot \hat{\mathbf{u}} \}, \end{aligned} \quad (2)$$

where

$$A_l = \frac{\omega_D^2}{\omega_D^2 + \omega_l^2} \left[1 + N(\omega_l) + i \left(\kappa(x_l, x_D) - \frac{\omega_l}{2\omega_D} \right) \right], \quad (3)$$

$$B_l = \frac{\omega_D^2}{\omega_D^2 + \omega_l^2} \left[N(\omega_l) + i \left(\kappa(x_l, x_D) + \frac{\omega_l}{2\omega_D} \right) \right], \quad (4)$$

with

$$\kappa(x_l, x_D) = -\left[\frac{1}{x_D} + 2 \sum_{n=1}^{\infty} \frac{x_l^2 - 2\pi x_D n}{(x_l + x_D)(x_l^2 + 4\pi^2 n^2)}\right] \quad (5)$$

and

$$x_D = \beta \hbar \omega_D, \quad x_l = \beta \hbar \omega_l, \quad \beta = 1/(k_B T), \quad n = 1, 2, 3, \dots \quad (6)$$

ω_D is the characteristic Debye frequency, k_B the Boltzmann constant, T the absolute temperature and $N(\omega_l)$ the occupation number of the rotator quantum level l (bosonic). A_l^* and B_l^* are the complex conjugates of A_l and B_l , respectively. ζ is the friction coefficient characterising the effects of the bath oscillator concentration on the rotator dynamics, I is the rotator moment of inertia.

We use the spherical harmonic expansion of the unit vector operator $\hat{\mathbf{u}}$ as [1, 2]

$$\hat{\mathbf{u}}(t) = \sum_{l=1}^{\infty} (\hat{\mathbf{u}}_l^+ + \hat{\mathbf{u}}_l^-(t)), \quad (7)$$

where

$$\hat{u}_{lx}^+(t) = \frac{1}{2} \sum_{m=-l}^l |l, m\rangle [\langle l-1, m+1 | A(l, m) - \langle l-1, m-1 | B(l, m)], \quad (8)$$

$$\hat{u}_{ly}^+(t) = \frac{1}{2i} \sum_{m=-l}^l |l, m\rangle [\langle l-1, m+1 | A(l, m) + \langle l-1, m-1 | B(l, m)], \quad (9)$$

$$\hat{u}_{lz}^+(t) = \sum_{m=-l}^l |l, m\rangle \langle l-1, m | C(l, m) \quad (10)$$

and

$$\hat{\mathbf{u}}_l^-(t) = (\hat{\mathbf{u}}_l^+(t))^\dagger. \quad (11)$$

$$A(l, m) = \sqrt{\frac{(l-m)(l-m-1)}{(2l-1)(2l+1)}}, \quad (12)$$

$$B(l, m) = \sqrt{\frac{(l+m)(l+m-1)}{(2l-1)(2l+1)}}, \quad (13)$$

$$C(l, m) = \sqrt{\frac{(l-m)(l+m)}{(2l-1)(2l+1)}}. \quad (14)$$

The a.c.-d.c. field coupling term is

$$\hat{H}_E(t) = \begin{cases} 0 & \text{if } t \leq 0 \\ -\mu(E_c + E_a \cos \omega t) \cos \hat{\beta} - \frac{\alpha_{\parallel} - \alpha_{\perp}}{2} (E_c + E_a \cos \omega t)^2 \cos^2 \hat{\beta} - \\ -\frac{\alpha_{\perp}}{2} (E_c + E_a \cos \omega t)^2 \hat{I} & \text{if } t > 0. \end{cases} \quad (15)$$

α_{\parallel} and α_{\perp} are, respectively, the rotator polarisability tensor components parallel and perpendicular to the molecular principal axis. We have assumed that the electric fields are applied along the z -axis of the laboratory frame. $\hat{\beta}$ is the angle between the applied field and the dipolar axis. With this Hamiltonian, the initial condition corresponds to equilibrium under free rotations, $\hat{\rho}(t=0) = \hat{\rho}_S^{eq} = \exp(-\frac{\hat{H}_S}{k_B T})/Z$ where Z is the rotator one particle partition function.

In a recent work [3], we used the Hounkonnou-Navez master equation [1] to verify the dielectric properties of a system of polar rotators in interaction with a constant electric field of strength E_c . The effects of inertia and bath concentration were intensively explored. Using the rotational Smoluchowski equation [4], Morita et al. [5] and Matsumoto et al. [6] presented studies of this problem but the former laid much interest on the effect of the applied field on the Kerr effect relaxation that results from the sudden application of the d.c. field. By averaging the Langevin equation, Coffey [7, 8, 9] tackled the

problem emphasising on the effect of inertia but his analysis was limited to the electrical susceptibility.

In the present work, we consider the effect of coupling a constant d.c. field with a radio frequency a.c. field. In the course of this work, we adopt the notations of paper III [3] so that we can directly exploit existing results therein. The polarisation and the Kerr functions can be calculated using the Hounkonnou-Titintah (HT) quantum relations [3]

$$P(t) = \frac{2\mu}{3} \sum_{l=0}^{\infty} (l+1) \frac{e^{-\beta E_l}}{Z} \text{Re} \sigma_{l,l+1}(t) \quad (16)$$

$$\Phi(t) = \frac{2}{15} \sum_{l=0}^{\infty} \frac{e^{-\beta E_l}}{Z} \frac{(l+1)}{(2l+3)} \left\{ \frac{l(2l+1)}{(2l-1)} \varphi_{l,l}(t) + 3(l+2) \text{Re} \eta_{l,l+2}(t) \right\}. \quad (17)$$

where Z is the one particle free rotator canonical partition function and Re denotes the real part. The reduced HT equations for the matrix elements $\sigma_{l,l+1}(t)$, $\varphi_{l,l}(t)$, and $\eta_{l,l+2}(t)$ [3] are:

i) the reduced HT1:

$$\begin{aligned} & \left(\frac{\partial}{\partial t} - \frac{i\hbar}{I} (l+1) \right) \sigma_{l,l+1}(t) + B \left[\left\{ \left(A_l^* l^2 + B_{l+1} (l+1)^2 \right) \frac{1}{2l+1} + (A_{l+1} (l+1)^2 \right. \right. \\ & \left. \left. + B_{l+2}^* (l+2)^2 \right) \frac{1}{2l+3} \right\} \sigma_{l,l+1}(t) - e^{\beta(E_l - E_{l-1})} \frac{l}{2l+1} \left[B_l l \right. \\ & \left. + (l+1) B_{l+1}^* \right] \sigma_{l-1,l}(t) (1 - \delta_{l0}) - e^{-\beta(E_{l+1} - E_l)} \frac{l+2}{2l+3} \left[A_{l+1}^* (l+1) \right. \\ & \left. + A_{l+2} (l+2) \right] \sigma_{l+1,l+2}(t) - \frac{l+1}{(2l+1)(2l+3)} \left[A_{l+1}^* (l+1) \right. \\ & \left. \left. + B_{l+1}^* (l+1) \right] \sigma_{l,l+1}^*(t) \right] = -i \frac{\mu E(t)}{\hbar} \left(1 - e^{-\beta(E_{l+1} - E_l)} \right); \end{aligned} \quad (18)$$

ii) the reduced HT2:

$$\begin{aligned}
& \frac{\partial}{\partial t} \varphi_{l,l}(t) + 2BRe \left\{ \frac{(A_l l^2 + B_{l+1}(l+1)^2)}{2l+1} \varphi_{l,l}(t) - A_{l+1}(l+1) \frac{(l+2)(2l-1)}{(2l+1)^2} \right. \\
& \times e^{-\beta(E_{l+1}-E_l)} \varphi_{l+1,l+1}(t) - B_l l \frac{(l-1)(2l+3)}{(2l+1)^2} e^{\beta(E_l-E_{l-1})} \varphi_{l-1,l-1}(t) (1-\delta_{l0}) \\
& \left. - 3 \frac{(B_l l + A_{l+1}(l+1))}{(2l+1)^2} e^{\beta(E_l-E_{l-1})} \eta_{l-1,l+1}(t) (1-\delta_{l0}) \right\} = \frac{\mu E(t)}{\hbar} \\
& \times \left(\frac{2l-1}{2l+1} Im \sigma_{l,l+1}(t) - e^{\beta(E_l-E_{l-1})} \frac{2l+3}{2l+1} Im \sigma_{l-1,l}(t) (1-\delta_{l,0}) \right) \quad (19)
\end{aligned}$$

and

iii) the reduced HT3:

$$\begin{aligned}
& \left[\frac{\partial}{\partial t} - \frac{i\hbar}{I} (2l+3) \right] \eta_{l,l+2}(t) + B \left[\left\{ [A_l^* l^2 + B_{l+1}(l+1)^2] \frac{1}{2l+1} + [A_{l+2}(l+2)^2 \right. \right. \\
& \left. \left. + B_{l+3}^*(l+3)^2 \right] \frac{1}{2l+5} \right\} \eta_{l,l+2}(t) - \frac{l}{2l+1} e^{\beta(E_l-E_{l-1})} \\
& \times [B_l^* l + B_{l+2}(l+2)] \eta_{l-1,l+1}(t) (1-\delta_{l0}) - e^{-\beta(E_{l+1}-E_l)} \frac{l+3}{2l+5} \\
& \times [A_{l+1}^*(l+1) + A_{l+3}(l+3)] \eta_{l+1,l+3}(t) - \frac{2}{(2l+1)(2l+5)} \\
& \times [A_{l+1}^*(l+1) + B_{l+2}(+2)] \varphi_{l+1,l+1}(t) \left. \right] = i \frac{\mu E(t)}{\hbar} \\
& \times \left(e^{-\beta(E_{l+1}-E_l)} \sigma_{l+1,l+2}(t) - \sigma_{l,l+1}(t) \right) - i \frac{\Delta \alpha E(t)^2}{2\hbar} \left(1 - e^{-\beta(E_{l+2}-E_l)} \right), \quad (20)
\end{aligned}$$

where $B = \zeta/I$. The initial conditions on these matrix elements are

$$\sigma_{l,l+1}(t=0) = \varphi_{l,l}(t=0) = \eta_{l,l+2}(t=0) = 0.$$

2 On the electrical susceptibility and the Kerr functions

In this section, the calculations of the electrical susceptibility and the Kerr functions are done in two different physical limits: 1) the classical Brownian limit and 2) the rotating wave approximation (RWA). In each case, we analyse the long time effect, that is, we consider times very long compared to the period of collision $\tau = 1/B$, the Debye relaxation time $\tau_D = \zeta/(2Ik_BT)$ and the mean thermal angular time $(I/k_BT)^{0.5}$.

2.1 The classical Brownian limit

This limit is characterised by slow moving rotators entering into instantaneous collisions with the bath of fast moving oscillators. Inertial effects are very important for understanding line shapes. With the aid of the Fokker-Planck-Kramer (FPK) equation [10, 11, 12, 13, 14], Hounkonnou et al. [13, 15, 16, 17] presented the steady state analysis of the electric polarisation and the Kerr optical function in a radio frequency a.c. field; while their electric susceptibility function was given as a continued fraction, the Kerr function was in the form of exponential integrals. Filippini [18] measured experimentally the Kerr dispersion constant when an a.c. field superimposed on a unidirectional field is applied to a liquid. Coffey and Paranjape [20], Morita [4], Morita and Watanabe [21], gave theoretical descriptions of these phenomena using pure classical diffusion equations.

The electrical susceptibility

In the classical limit, quantum equations reduce to the classical HT equations for the electrical susceptibility [3]

$$P(\tau) = \frac{\mu}{3} S_0^0(\tau), \quad (21)$$

$$\left(\frac{d}{d\tau} + 2j\right) S_j^0(\tau) + 2b_2 \left[(j+1) S_j^1(\tau) - j S_{j-1}^1(\tau)\right] = 0 \quad (22)$$

and

$$\left(\frac{d}{d\tau} + 2j + 1\right) S_j^1(\tau) - b_1 \left[S_j^0(\tau) - S_{j+1}^0(\tau)\right] = -b_1 \frac{\mu E_a}{k_B T} (r + \cos \omega t) \delta_{j,0}, \quad (23)$$

where $\tau = Bt$, $\omega' = \omega/B$ are dimensionless time and frequency, respectively; $r = E_c/E_a$ measures the ratio of the constant field strength to the amplitude of the a.c. field. $b_1 b_2 = \gamma = Ik_B T/\zeta^2$, where ζ is the coupling coefficient. In the steady state regime, we search for $S_j^m(\tau)$ in the forms:

$$\begin{aligned} S_0^0(\omega', \tau) &= \frac{\mu E_a}{k_B T} \left[r + S_0^{0'}(\omega') e^{i\omega' \tau} + (S_0^{0'}(\omega'))^* e^{-i\omega' \tau} \right], \\ S_j^0(\omega', \tau) &= \frac{\mu E_a}{k_B T} S_j^{0'}(\omega') e^{i\omega' \tau} + C.C. \text{ for } j \neq 0, \\ S_j^1(\omega', \tau) &= \frac{\mu E_a}{k_B T} S_j^{1'}(\omega') e^{i\omega' \tau} + C.C. \text{ for all } j. \end{aligned} \quad (24)$$

On substituting these into the hierarchy (22) -(23) and solving for $S_0^{0'}(\omega')$, we get

$$S_0^{0'}(\omega') = \frac{\gamma}{2\gamma + i\omega' \left[1 + i\omega' + \frac{2\gamma}{2 + i\omega' + \frac{4\gamma}{3 + i\omega' + \frac{4\gamma}{4 + i\omega' + \frac{6\gamma}{5 + i\omega' + \dots}}}} \right]} \quad (25)$$

and using (21), we deduce the polarisation

$$P(\omega', \tau) = \frac{\mu^2 E_a}{3k_B T} \left\{ \frac{r}{2} + \frac{\gamma e^{i\omega' \tau}}{2\gamma + i\omega' \left[1 + i\omega' + \frac{2\gamma}{2 + i\omega' + \frac{4\gamma}{3 + i\omega' + \frac{4\gamma}{4 + i\omega' + \dots}}}} \right]} + C.C. \right\}. \quad (26)$$

In the absence of the d.c. field ($r = 0$), the result of Gross [22] on generalised Brownian motion is recovered. We define a reduced susceptibility $\chi_r(\omega', \tau)$ as

$$\chi_r(\omega', \tau) = r + 2 | S_0^{0'}(\omega') | \cos(\omega\tau - \alpha(\omega')), \quad (27)$$

where $\alpha(\omega,)$, the phase difference between the exciting a.c. field and the dielectric response function (the polarisation), furnishes valuable informations on the absorption properties of the medium under investigation. It is given by

$$\tan \alpha(\omega') = -\frac{Im S_0^{0'}(\omega')}{Re S_0^{0'}(\omega')}. \quad (28)$$

On neglecting inertial effects in (25), we obtain the Debye limit

$$S_0^{0'}(\omega') = \frac{1}{2(1 + i\omega\tau_D)} \quad (29)$$

in usual frequency units. In this case, the phase is given by $\tan \alpha(\omega) = \omega \tau_D$ with $\tau_D = \zeta/(2k_B T)$. The lowest inertial limit, corresponding to the Rocard formula,

$$S_0^{0'}(\omega') = \frac{1}{2(1 + i\omega \tau_D - (I\omega^2/2k_B T))} \quad (30)$$

leads to the phase expression $\tan \alpha(\omega) = \omega \tau_D / (1 - (I\omega^2/2k_B T))$ which yields a maximum phase of $\pi/2$ for frequency of $\sqrt{2}$ times mean thermal agitation frequency ($\omega_{mean} = (k_B T/I)^{0.5}$). At this frequency value, the rate of energy absorption from the surrounding bath by the rotators is in phase with the forcing field (since the rate of heat exchange between the rotator and the surrounding is proportional to minus the rate of change of the induced polarisation [2, 3, 19]). On defining a new dimensionless frequency $\nu = \omega/\omega_{mean}$ in (25), we rewrite $S_0^{0'}$ as

$$S_0^{0'}(\nu) = \frac{1}{2 + i\nu/\sqrt{\gamma} - \nu^2 + \frac{2i\sqrt{\gamma}\nu}{2 + i\sqrt{\gamma}\nu + \frac{4\gamma}{3 + i\sqrt{\gamma}\nu + \frac{4\gamma}{4 + i\sqrt{\gamma}\nu + \dots}}}}. \quad (31)$$

Figures 1 and 2 show the plots of the external exciting field $\cos \nu t'$ and those of the reduced susceptibility $\chi_r(\omega', \tau)$ as functions of the dimensionless time τ (with $\tau = t\omega_{mean}$) for $\nu = 0.15, 4.00$ and for different values of γ . For fixed ω_{mean} , we analyse the effect of friction ζ on the phase, through $\gamma = Ik_B T/\zeta^2$. Figure 3 shows a 3-D plot of $\chi_r(\omega', \tau)$ for $\gamma = 0.05$. Figure 4 shows a 3-D plot of the tangent of the phase angle as a function of the reduced frequency ν and γ . The resonance peaks are found to shift towards larger frequency values as γ increases. It is important to note that while the Debye theory

predicts such resonances only for infinite frequencies ($\tan \alpha(\omega) = \omega \tau_D$) and the Rocard lowest inertial limit predicts a resonance at $\nu = \sqrt{2}$, our results extensively portrays the effect of inertia on this resonance.

The Kerr function

The classical HT equations [3] for the optical Kerr function are:

$$\Phi(\tau) = \frac{1}{30} Y_0^0(\tau) \quad (32)$$

with

$$\begin{aligned} & \left(\frac{d}{d\tau} + 2j \right) Y_j^0(\tau) + 24b_2 \left((j+1)Y_j^1(\tau) - jY_{j-1}^1(\tau) \right) \\ &= -4b_2 \frac{\mu E_a}{k_B T} (r + \cos \omega' \tau) S_{j-1}^1(\tau) (1 - \delta_{j,0}), \end{aligned} \quad (33)$$

$$\begin{aligned} & \left(\frac{d}{d\tau} + 2j+1 \right) Y_j^1(\tau) - \frac{b_1}{3} \left(Y_j^0(\tau) - Y_{j+1}^0(\tau) \right) + \frac{b_1}{3} \left(X_j(\tau) - X_{j+1}(\tau) \right) \\ &= -b_1 \frac{\mu E_a}{k_B T} (r + \cos \omega' \tau) S_j^0(\tau) - b_1 \frac{\Delta \alpha E_a^2}{k_B T} (r + \cos \omega' \tau)^2 \delta_{j,0}, \end{aligned} \quad (34)$$

$$\begin{aligned} & \left[(2j+1) \left(\frac{d}{d\tau} + 2j \right) + 2 \right] X_j(\tau) - j \left(\frac{d}{d\tau} + 2j-2 \right) X_{j-1}(\tau) \\ & - (j+1) \left(\frac{d}{d\tau} + 2j+2 \right) X_{j+1}(\tau) - \frac{1}{2} Y_j^0(\tau) = b_2 \frac{\mu E_a}{k_B T} (r + \cos \omega' \tau) \\ & \times \left[-2j(j-1) S_{j-2}^1(\tau) + j(4j+5) S_{j-1}^1(\tau) - (j+1)(2j+3) S_j^1(\tau) \right]. \end{aligned} \quad (35)$$

Steady state solutions are sought in the forms:

$$X_j(\omega', \tau) = \left(\frac{\mu E_a}{k_B T} \right)^2 \left[X_{j,0}(\omega') + X_{j,1}(\omega') e^{i\omega' \tau} + X_{j,2}(\omega') e^{2i\omega' \tau} + C.C. \right],$$

$$\begin{aligned}
Y_j^0(\omega', \tau) &= \left(\frac{\mu E_a}{k_B T}\right)^2 \left[Y_{j,0}^0(\omega') + Y_{j,1}^0(\omega') e^{i\omega' \tau} + Y_{j,2}^0(\omega') e^{2i\omega' \tau} + C.C. \right], \\
Y_j^1(\omega', \tau) &= \left(\frac{\mu E_a}{k_B T}\right)^2 \left[Y_{j,0}^1(\omega') + Y_{j,1}^1(\omega') e^{i\omega' \tau} + Y_{j,2}^1(\omega') e^{2i\omega' \tau} + C.C. \right], \quad (36)
\end{aligned}$$

where C.C. denotes complex conjugate. Knowing the forms of S_j^m , we obtain the three systems of hierarchies (each system being a set of three coupled equations (triplets)):

t1)

$$\begin{aligned}
&2jY_{j,0}^0(\omega') + 24b_2 \left((j+1)Y_{j,0}^1(\omega') - jY_{j-1,0}^1(\omega') \right) = -2b_2 S_{j-1}^1(\omega') (1 - \delta_{j,0}), \\
&(2j+1)Y_{j,0}^1(\omega') - \frac{b_1}{3} \left(Y_{j,0}^0(\omega') - Y_{j+1,0}^0(\omega') \right) + \frac{b_1}{3} \left(X_{j,0}(\omega') - X_{j+1,0}(\omega') \right) \\
&= -\frac{b_1}{4} \left[(2r^2 + 2r^2/R + 1/R) \delta_{j,0} + 2S_j^0(\omega') \right], \\
&\left[2j(2j+1) + 2 \right] X_{j,0}(\omega') - j(2j-2)X_{j-1,0}(\omega) - (j+1)(2j+2)X_{j+1,0}(\omega') \\
&- 1/2Y_{j,0}^0(\omega') = \frac{b_2}{2} \left[-2j(j-1)S_{j-2}^1(\omega') + j(4j+5)S_{j-1}^1(\omega') \right. \\
&\left. - (j+1)(2j+3)S_j^1(\omega') \right]; \quad (37)
\end{aligned}$$

t2)

$$\begin{aligned}
&(i\omega' + 2j)Y_{j,1}^0(\omega') + 24b_2 \left((j+1)Y_{j,1}^1(\omega') - jY_{j-1,1}^1(\omega') \right) \\
&= -4rb_2 S_{j-1}^1(\omega') (1 - \delta_{j,0}), \\
&(i\omega' + 2j+1)Y_{j,1}^1(\omega') - \frac{b_1}{3} \left(Y_{j,1}^0(\omega') - Y_{j+1,1}^0(\omega') \right) \\
&+ \frac{b_1}{3} \left(X_{j,1}(\omega') - X_{j+1,1}(\omega') \right) = -r \frac{b_1}{4} \left[(2 + 4/R) \delta_{j,0} + 4S_j^0 \right], \\
&\left[(2j+1)(i\omega' + 2j) + 2 \right] X_{j,1}(\omega') - j(i\omega' + 2j-2)X_{j-1}(\omega') \\
&- (j+1)(i\omega' + 2j+2)X_{j+1,1}(\omega') - (1/2)Y_{j,1}^0(\omega') = b_2 r \left[-2j(j-1)S_{j-2}^1(\omega') \right.
\end{aligned}$$

$$+j(4j+5)S_{j-1}^1(\omega') - (j+1)(2j+3)S_j^1(\omega') \Big] \quad (38)$$

and

t3)

$$\begin{aligned} & (2i\omega' + 2j)Y_{j,2}^0(\omega') + 24b_2 \left((j+1)Y_{j,2}^1(\omega') - jY_{j-1,2}^1(\omega') \right) \\ &= -2b_2 S_{j-1}^1(\omega') (1 - \delta_{j,0}), \\ & (2i\omega' + 2j + 1)Y_{j,2}^1(\omega') - \frac{b_1}{3} (Y_{j,2}^0(\omega') - Y_{j+1,2}^0(\omega')) \\ &+ \frac{b_1}{3} (X_{j,2}(\omega') - X_{j+1,2}(\omega')) = -\frac{b_1}{4} \left[\frac{1}{R} \delta_{j,0} + 2S_j^0 \right], \\ & \left[(2j+1)(2i\omega' + 2j) + 2 \right] X_{j,2}(\omega') - j(2i\omega' + 2j - 2) X_{j-1,2}(\omega') \\ & - (j+1)(2i\omega' + 2j + 2) X_{j+1,2}(\omega') - \frac{1}{2} Y_{j,2}^0(\omega') = \frac{b_2}{2} \left[-2j(j-1)S_{j-2}^1(\omega') \right. \\ & \left. + j(4j+5)S_{j-1}^1(\omega') - (j+1)(2j+3)S_j^1(\omega') \right], \end{aligned} \quad (39)$$

where $R = \mu^2/(\Delta\alpha k_B T)$. For simplicity, we have left out the primes on each S_j^m . i denotes the complex number $\sqrt{-1}$.

The technique adopted in solving these triplets is based on convergents. Remark that the above systems could be written in matrix forms of infinite dimensions. The notion of convergence can be seen as limiting the dimensions of the matrices. The zeroth convergent consists of considering only equations involving just $j = 0$. The first convergent is the modification of the zeroth by including $j = 1$ terms. The former is the solution of a 3×3 matrix equation, while the latter is that of a 6×6 matrix equation. Reliable spectral informations can only be got from at least a 6×6 matrix equation. The following are the

expressions for $Y_{0,0}^0(\omega')$, $Y_{0,1}^0(\omega')$ and $Y_{0,2}^0(\omega')$ obtained for $j = 1$:

$$\begin{aligned}
Y_{0,0}^0(\omega') = & \frac{1}{2}(\alpha + 2r - \alpha r) + (1 - \alpha)(1 - r) \left\{ \left(1 - \frac{i\omega'}{2}\right) \right. \\
& + \frac{2i\omega'}{3(2 + 5\gamma)} \left[2 - \gamma - \frac{8\gamma}{2 + i\omega' + \frac{4\gamma}{3 + i\omega' + \frac{4\gamma}{4 + i\omega' + \dots}}} \right. \\
& + \frac{4\gamma^2/3}{4\gamma + (2 + i\omega') \left(3 + i\omega' + \frac{4\gamma}{4 + i\omega' + \frac{6\gamma}{5 + i\omega' + \frac{6\gamma}{6 + i\omega' + \dots}}} \right)} \left. \right] \left. \right\} \\
& \times \frac{\gamma}{2\gamma + i\omega' \left(1 + i\omega' + \frac{2\gamma}{2 + i\omega' + \frac{4\gamma}{3 + i\omega' + \frac{4\gamma}{4 + i\omega' + \dots}}} \right)} \\
& + \frac{64}{9} \frac{\gamma}{2 + 5\gamma} Y_{2,0}^0(\omega'), \tag{40}
\end{aligned}$$

$$\begin{aligned}
Y_{0,1}^0(\omega') = & \sqrt{r(1 - r)} \left\{ (1 + 2/R) \frac{6\gamma(1 + \alpha)}{1 + i\omega'} \left(2 + i\omega' + 4\gamma \frac{15 + 4i\omega'}{(3 + i\omega')(4 + i\omega')} \right) \right. \\
& + (1 - \alpha) \left[\frac{24\gamma}{(1 + i\omega')(2 + i\omega')} \left(2 + i\omega' + 4\gamma \frac{15 + 4i\omega'}{(3 + i\omega')(4 + i\omega')} \right) \right. \\
& + \frac{8i\omega'\gamma}{1 + i\omega'} - \frac{32i\omega'\gamma^2}{(1 + i\omega')(3 + i\omega')(4 + i\omega')} \left(\frac{6(1 + i\omega')}{(2 + i\omega')} \right. \\
& - \left. \left. \frac{4\gamma}{4\gamma + (2 + i\omega') \left(3 + i\omega' + \frac{4\gamma}{4 + i\omega' + \frac{6\gamma}{5 + i\omega' + \frac{6\gamma}{6 + i\omega' + \dots}}} \right)} \right) \right] -
\end{aligned}$$

$$\begin{aligned}
& - \frac{192\gamma^2 i\omega'}{(1+i\omega')(3+i\omega')\left(2+i\omega'+\frac{4\gamma}{3+i\omega'+\frac{4\gamma}{4+i\omega'+\frac{6\gamma}{5+i\omega'+\dots}}}\right)} \Bigg] \\
& \times \frac{\gamma}{2\gamma+i\omega'\left(1+i\omega'+\frac{2\gamma}{2+i\omega'+\frac{4\gamma}{3+i\omega'+\frac{4\gamma}{4+i\omega'+\dots}}}\right)} \\
& + \frac{128\gamma^2/r}{3+i\omega'} Y_{2,1}^0(\omega') \Bigg\} / \left\{ \left(i\omega' + 4\gamma \frac{3+i\omega'}{(1+i\omega')(2+i\omega')} \right) (2+i\omega' \right. \\
& + 4\gamma \frac{15+4i\omega'}{(3+i\omega')(4+i\omega')}) + \frac{8i\omega'\gamma}{1+i\omega'} \\
& \left. - \frac{32i\omega'\gamma^2}{(1+i\omega')(2+i\omega')(3+i\omega')(4+i\omega')} \right\}, \tag{41}
\end{aligned}$$

$$\begin{aligned}
Y_{0,2}^0(\omega') = & (1-r) \left\{ \frac{3\gamma\alpha}{1+2i\omega'} \left(2+2i\omega' + 4\gamma \frac{15+8i\omega'}{(3+2i\omega')(4+2i\omega')} \right) \right. \\
& + (1-\alpha) \left[6\gamma \frac{2+i\omega'}{(1+2i\omega')(2+2i\omega')} \left(2+2i\omega' + 4\gamma \frac{15+8i\omega'}{(3+2i\omega')(4+2i\omega')} \right) \right. \\
& + \frac{8i\omega'\gamma}{1+2i\omega'} - \frac{96i\omega'\gamma^2}{(1+2i\omega')(3+2i\omega')\left(2+i\omega'+\frac{4\gamma}{3+i\omega'+\frac{4\gamma}{4+i\omega'+\dots}}}\right)} \\
& \left. \left(3 - \frac{4\gamma}{4\gamma+(2+i\omega')\left(3+i\omega'+\frac{4\gamma}{4+i\omega'+\dots}\right)} + 6i\omega' \right) \right] \\
& - 16i\omega'\gamma^2 \frac{\gamma}{(1+2i\omega')(2+2i\omega')(3+2i\omega')(4+2i\omega')} \Bigg] \\
& \times \frac{\gamma}{2\gamma+i\omega'\left(1+i\omega'+\frac{2\gamma}{2+i\omega'+\frac{4\gamma}{3+i\omega'+\frac{4\gamma}{4+i\omega'+\dots}}}\right)} + \\
& + \frac{128\gamma^2}{(1+2i\omega')(3+2i\omega')} Y_{2,2}^0(\omega') \Bigg\} / \left\{ \left[2i\omega' + 4\gamma \frac{3+4i\omega'}{(1+2i\omega')(2+2i\omega')} \right] \times \right.
\end{aligned}$$

$$\begin{aligned}
& \times \left[2 + 2i\omega' + 4\gamma \frac{15 + 8i\omega'}{(3 + 2i\omega')(4 + 2i\omega')} \right] \\
& + \frac{16i\omega'\gamma \left((2 + i\omega')(3 + i\omega')(4 + i\omega') - 4\gamma \right)}{(1 + 2i\omega')(2 + 2i\omega')(3 + 2i\omega')(4 + 2i\omega')} \Big\}. \quad (42)
\end{aligned}$$

We can now write the Kerr function as

$$\Phi(\omega', \tau) = \frac{1}{30} E^2 K_0 \left[Y_{0,0}^0(\omega') + Y_{0,1}^0(\omega') \exp(i\omega' \tau) + Y_{0,2}^0(\omega') \exp(2i\omega' \tau) + C.C. \right], \quad (43)$$

where $E^2 = E_a^2 + E_c^2$ and $K_0 = \left(\frac{\mu}{k_B T} \right)^2 + \frac{\Delta\alpha}{k_B T}$. Remark that in the last expressions we have replaced the field parameter $r = E_c/E_a$ with a more convenient one $r = E_c^2/E^2$ and the quantity R is replaced by $\alpha = \frac{\Delta\alpha/(k_B T)}{K_0}$. With these new parameters, the limiting cases are better understood, for example $r = 0$ corresponds to pure a.c. field effects and $\alpha = 0$ demonstrates the properties of a non polarisable but polar molecule. Note that both parameters are such that $0 \leq r \leq 1$ and $0 \leq \alpha \leq 1$. The Kerr function (eq.42) presents very interesting properties. It expresses the time, radio frequency (rf), rotator-bath parameters and more importantly the E_c/E_a dependences of the Kerr electrical birefringence (KEB). For infinitely high frequencies, the function reduces to the constant field steady state expression

$$\Phi_\infty = \frac{E_c^2}{15} \left(\left(\frac{\mu^2}{k_B T} \right)^2 + \frac{\Delta\alpha}{k_B T} \right) + \frac{E_a^2}{30} \frac{\Delta\alpha}{k_B T}. \quad (44)$$

The effect of the a.c. field is felt only when $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp} \neq 0$. This result is consistent with that of Doi and Edwards [23]. At very high frequencies, a.c. field effects on dipole

moments average out. Also, in the absence of the d.c. field ($r = 0$), the term $Y_{0,1}^0(\omega')$ vanishes and the result for pure a.c. field is recovered.

2.2 The rotating wave approximation (RWA) limit

In this limit, the solution of the rotators in the bath is assumed highly diluted, the pressure and friction are very low. The coupling parameter B or the characteristic rotator-bath frequency is very small compared to the rotator lines $\omega_l = (\hbar l/I)$. The dynamics of the rotator is mainly governed by free rotations and interactions with the re-orienting fields. Bath coupling affects only the frequency shifts and line widths. The absorption lines are the neat spectral lines corresponding to the different l transitions owing to non negligible Planck constant \hbar and finite inertia [22]. The transition frequencies are

$$\omega_{l \rightarrow l \pm \Delta l} = | (E_{l \pm \Delta l} - E_l) | / \hbar = (2l + 1 + \Delta l) \hbar / 2I$$

for transitions from l to $l \pm \Delta l$. At the level of linear response, $\Delta l = 1$ and $\omega_{l+1} = (l+1)\hbar/I$. For the lowest order nonlinear effect (the Kerr effect to the second order in electric field), $\Delta l = 2$ and $\omega_{2l+3} = (2l+3)\hbar/I$.

The relevant dielectric matrix elements are governed by the quantum HT equations for the electrical susceptibility and the Kerr optical functions [3]:

$$\left(\frac{\partial}{\partial t} - i(\omega_{l+1} + \Delta\omega_{l+1}) + \Gamma_{l+1} \right) \sigma_{l,l+1}(t) = -i \frac{\mu E_a}{\hbar} (r + \cos \omega t) \left(1 - e^{-\beta(E_{l+1} - E_l)} \right), \quad (45)$$

$$\left(\frac{\partial}{\partial t} + \gamma_l\right)\varphi_{l,l}(t) = \frac{\mu E_a}{\hbar}(r + \cos \omega t) \left(\frac{2l-1}{2l+1} \text{Im}\sigma_{l,l+1}(t) - e^{\beta(E_l - E_{l-1})} \frac{2l+3}{2l+1} \text{Im}\sigma_{l-1,l}(t)(1 - \delta_{l,0}) \right), \quad (46)$$

$$\begin{aligned} \left(\frac{\partial}{\partial t} - i(\omega_{2l+3} + \Delta\omega_{2l+3}) + \Gamma_{2l+3}\right)\eta_{l,l+2}(t) &= i\frac{\mu E_a}{\hbar}(r + \cos \omega t) \left(e^{-\beta(E_{l+1} - E_l)} \sigma_{l+1,l+2}(t) \right. \\ &\left. - \sigma_{l,l+1}(t) \right) - i\frac{\Delta\alpha E_a^2}{2\hbar}(r + \cos \omega t)^2 \left(1 - e^{-\beta(E_{l+2} - E_l)} \right). \end{aligned} \quad (47)$$

Here, we define the dimensionless line widths and frequency shifts:

$$\gamma'_l = \frac{I}{\hbar}\gamma_l = \frac{2BI}{\hbar} \frac{1}{2l+1} \left[l^2 \left(1 + \frac{1}{e^{\beta\hbar\omega_l} - 1} \right) + \frac{(l+1)^2}{e^{\beta\hbar\omega_{l+1}} - 1} \right], \quad (48)$$

$$\Gamma'_{l+1} = \frac{1}{2}(\gamma'_l + \gamma'_{l+1}), \quad (49)$$

$$\Gamma'_{2l+3} = \frac{1}{2}(\gamma'_l + \gamma'_{l+2}), \quad (50)$$

$$\begin{aligned} \Delta\omega'_{l+1} &= -\frac{4\hbar^3 B}{Ik_B^2 T^2} (2l+3) \sum_{n=0}^{\infty} \frac{(2n\pi)^3}{[(2n\pi)^2 + (al)^2]} \\ &\quad \times \frac{1}{[(2n\pi)^2 + (a(l+1))^2][(2n\pi)^2 + (a(l+2))^2]} \end{aligned} \quad (51)$$

and

$$\begin{aligned} \Delta\omega'_{2l+3} &= -\frac{4\hbar^3 B}{Ik_B^2 T^2} (2l+3) \sum_{n=0}^{\infty} \frac{(2n\pi)^5 \left(1 + \frac{a}{(n\pi)^2} (l^2 + 3l + 3) \right)}{[(2n\pi)^2 + (al)^2][(2n\pi)^2 + (a(l+1))^2]} \\ &\quad \times \frac{1}{[(2n\pi)^2 + (a(l+2))^2][(2n\pi)^2 + (a(l+3))^2]}, \end{aligned} \quad (52)$$

where $a = \hbar^2 / I k_B T$. These functions will indicate how line widths and frequency shifts respond to changing physical parameters like inertia, friction and temperature, thus their utility in exploring the influence of the parameter variations on spectral lines. Note that, in our dimensionless frequency units, we define the quantum state frequency $\omega'_l = l$.

The electrical susceptibility

We are interested in the steady state regime. On solving equation (45) for this, we get

$$\begin{aligned} \sigma_{l,l+1}^{st}(\omega, t) = & (\mu E_a / \hbar) \left(1 - \exp \left[-\frac{\hbar^2}{I k_B T} (l+1) \right] \right) \left\{ \frac{r}{\omega_{l+1} + \Delta\omega_{l+1} + i\Gamma_{l+1}} \right. \\ & \left. + \frac{e^{i\omega t}}{2(\omega_{l+1} + \Delta\omega_{l+1} - \omega + i\Gamma_{l+1})} + \frac{e^{-i\omega t}}{2(\omega_{l+1} + \Delta\omega_{l+1} + \omega + i\Gamma_{l+1})} \right\}. \end{aligned} \quad (53)$$

The polarisation is deduced as

$$\begin{aligned} P(\omega, t) = & \frac{\mu^2 E_a}{3k_B T} \sum_{l=0}^{\infty} \left(e^{-\beta E_l} - e^{-\beta E_{l+1}} \right) \frac{l+1}{a} \left(l+1 + \Delta\omega'_{l+1} \right) \\ & \times \left\{ r / \left[\left(l+1 + \Delta\omega'_{l+1} \right)^2 + \Gamma_{l+1}'^2 \right] + \left(\left[\left(l+1 + \Delta\omega'_{l+1} \right)^2 - \omega'^2 + \Gamma_{l+1}'^2 \right] \cos \omega t \right. \right. \\ & \left. \left. + 2\Gamma_{l+1}' \omega' \sin \omega t \right) / \left(\left[\left(l+1 + \Delta\omega'_{l+1} \right)^2 - \omega'^2 + \Gamma_{l+1}'^2 \right]^2 + 4\omega'^2 \Gamma_{l+1}'^2 \right) \right\}. \end{aligned} \quad (54)$$

These are the Van Vleck-Weisskopf line forms for the electrical susceptibility. Sharp separate lines result for small widths at half heights Γ_{l+1} . For line coupling and subsequent line overlaps to be absent, thus, Γ_{l+1} should be small compared to line spacings which for the electrical susceptibility stands at \hbar/I . Remark that the Boltzmann weight $e^{-\beta E_l}$ appearing in the last expression renders small quantum number transitions more probable. An appropriate Taylor expansion of the Bose-Einstein factor appearing in the expression

of the half width shows that a necessary condition for dominant lines is expressed by the inequality $(B/\omega_{mean})^2 \ll a^3/4 = (\hbar^2/Ik_BT)^3/4$.

For $r = 0$, we define the reduced susceptibility

$$\chi_r(\omega, t) = \cos(\omega t - \alpha(\omega)) \quad (55)$$

where $\alpha(\omega)$, the phase difference between the exciting field and the induced polarisation, is given by

$$\begin{aligned} \tan \alpha(\omega) = & \left[\sum_{l=0}^{\infty} (e^{-\beta E_l} - e^{-\beta E_{l+1}}) (l+1) (l+1 + \Delta\omega'_{l+1}) \Gamma'_{l+1} \omega' / \right. \\ & \left. \left(\left[(l+1 + \Delta\omega'_{l+1})^2 - \omega'^2 + \Gamma_{l+1}^{\prime 2} \right]^2 + 4\omega'^2 \Gamma_{l+1}^{\prime 2} \right) \right] / \\ & \left[\sum_{l=0}^{\infty} (e^{-\beta E_l} - e^{-\beta E_{l+1}}) (l+1) (l+1 + \Delta\omega'_{l+1}) \left((l+1 + \Delta\omega'_{l+1})^2 \right. \right. \\ & \left. \left. - \omega'^2 + \Gamma_{l+1}^{\prime 2} \right) / \left(\left[(l+1 + \Delta\omega'_{l+1})^2 - \omega'^2 + \Gamma_{l+1}^{\prime 2} \right]^2 + 4\omega'^2 \Gamma_{l+1}^{\prime 2} \right) \right]. \quad (56) \end{aligned}$$

Note that for usual temperatures and simple linear molecules like HCl and DCl [24, 25], the frequency shift has a negligible contribution as it varies as $\Delta\omega'_{l+1} \sim -10^{-4}(2l+3)$ compared to the corresponding line $l+1$.

The Kerr function

On using the expression for $\sigma_{l,l+1}^{st}(\omega, t)$ (equation (53)) into equations (46) and (47) and solving the resulting equations for the steady state matrix elements $\varphi_{l,l}^{st}(\omega, t)$ and $\eta_{l,l+2}^{st}(\omega, t)$, we deduce that the Kerr function comprises three terms: a frequency dependent time constant term $\Phi_0(\omega)$, an ω -frequency time dependent term $\Phi_1(\omega)e^{i\omega t}$ and a

2ω - frequency time dependent one $\Phi_2(\omega)e^{2i\omega t}$ with their respective complex conjugates.

In other words,

$$\Phi(\omega, t) = \Phi_0(\omega) + \Phi_1(\omega)e^{i\omega t} + \Phi_2(\omega)e^{2i\omega t} + C.C., \quad (57)$$

where

$$\begin{aligned} \Phi_0(\omega') = & \frac{1}{60}E^2K_0 \sum_{l=0}^{\infty} \frac{l+1}{a} \left[(1-\alpha) \frac{l}{2l-1} \frac{1}{\gamma'_l} (e^{-\beta E_{l-1}} - e^{-\beta E_l}) \right. \\ & \times \left(2r \frac{\Gamma'_l + i(l + \Delta\omega'_l)}{(l + \Delta\omega'_l)^2 + \Gamma_l'^2} + \frac{1}{2}(1-r) \frac{\Gamma'_l + i(l + \Delta\omega'_l - \omega')}{(l + \Delta\omega'_l - \omega')^2 + \Gamma_l'^2} \right) \\ & - \frac{l}{2l+3} (1-\alpha) \frac{1}{\gamma'_l} (e^{-\beta E_l} - e^{-\beta E_{l+1}}) \left(2r \frac{\Gamma'_{l+1} + i(l+1 + \Delta\omega'_{l+1})}{(l+1 + \Delta\omega'_{l+1})^2 + \Gamma_{l+1}'^2} \right. \\ & \left. \left. + \frac{1}{2}(1-r) \frac{\Gamma'_{l+1} + i(l+1 + \Delta\omega'_{l+1} - \omega')}{(l+1 + \Delta\omega'_{l+1} - \omega')^2 + \Gamma_{l+1}'^2} \right) + \frac{3(l+2)}{2l+3} \frac{1}{(2l+3 + \Delta\omega'_{2l+3})^2 + \Gamma_{2l+3}'^2} \right. \\ & \times \left\{ (2l+3 + \Delta\omega'_{2l+3}) - i\Gamma'_{2l+3} \right\} \left[(e^{-\beta E_l} - e^{-\beta E_{l+1}}) \right. \\ & \times \left(2r \frac{(l+1 + \Delta\omega'_{l+1} - i\Gamma'_{l+1})}{(l+1 + \Delta\omega'_{l+1})^2 + \Gamma_{l+1}'^2} + \frac{1}{2}(1-r) \frac{(l+1 + \Delta\omega'_{l+1} - \omega' - i\Gamma'_{l+1})}{(l+1 + \Delta\omega'_{l+1} - \omega')^2 + \Gamma_{l+1}'^2} \right. \\ & \left. \left. + \frac{1}{2}(1-r) \frac{(l+1 + \Delta\omega'_{l+1} + \omega' - i\Gamma'_{l+1})}{(l+1 + \Delta\omega'_{l+1} + \omega')^2 + \Gamma_{l+1}'^2} \right) - (e^{-\beta E_{l+1}} - e^{-\beta E_{l+2}}) \right. \\ & \times \left(2r \frac{(l+2 + \Delta\omega'_{l+2} - i\Gamma'_{l+2})}{(l+2 + \Delta\omega'_{l+2})^2 + \Gamma_{l+2}'^2} + \frac{1}{2}(1-r) \frac{(l+2 + \Delta\omega'_{l+2} - \omega' - i\Gamma'_{l+2})}{(l+2 + \Delta\omega'_{l+2} - \omega')^2 + \Gamma_{l+2}'^2} \right. \\ & \left. \left. + \frac{1}{2}(1-r) \frac{(l+2 + \Delta\omega'_{l+2} + \omega' - i\Gamma'_{l+2})}{(l+2 + \Delta\omega'_{l+2} + \omega')^2 + \Gamma_{l+2}'^2} \right) \right] (1-\alpha) \\ & \left. + \frac{\alpha}{2} (e^{-\beta E_l} - e^{-\beta E_{l+2}}) (2l+3 + \Delta\omega'_{2l+3}) \right\}, \quad (58) \end{aligned}$$

$$\begin{aligned} \Phi_1(\omega') = & \frac{\sqrt{r(1-r)}}{60} E^2 K_0 \sum_{l=0}^{\infty} \frac{l+1}{a} \left[\frac{2(1-\alpha)(\gamma'_l - i\omega')}{\gamma_l'^2 + \omega'^2} \left\{ \frac{l}{2l+3} (e^{-\beta E_l} - e^{-\beta E_{l+1}}) \right. \right. \\ & \times \left(\frac{\Gamma'_{l+1}}{(l+1 + \Delta\omega'_{l+1})^2 + \Gamma_{l+1}'^2} + \frac{\Gamma'_{l+1} + i(l+1 + \Delta\omega'_{l+1} + \omega')}{(l+1 + \Delta\omega'_{l+1} + \omega')^2 + \Gamma_{l+1}'^2} - \right. \end{aligned}$$

$$\begin{aligned}
& -\frac{\Gamma'_{l+1} + i(l+1 + \Delta\omega'_{l+1} - \omega')}{(l+1 + \Delta\omega'_{l+1} - \omega')^2 + \Gamma'^2_{l+1}} \Big) - \frac{l}{2l-1} (e^{-\beta E_{l-1}} - e^{-\beta E_l}) \\
& \times \left(\frac{\Gamma'_l}{(l + \Delta\omega'_l)^2 + \Gamma'^2_l} + \frac{\Gamma'_l + i(l + \Delta\omega'_l + \omega')}{(l + \Delta\omega'_l + \omega')^2 + \Gamma'^2_l} \right. \\
& \left. - \frac{\Gamma'_l + i(l + \Delta\omega'_l - \omega')}{(l + \Delta\omega'_l - \omega')^2 + \Gamma'^2_l} \right) \Big\} + \frac{3(l+2)}{2l+3} \\
& \times \frac{(2l+3 + \Delta\omega'_{2l+3})^2 - \omega'^2 - 2i\omega'\Gamma'_{2l+3}}{\left[(2l+3 + \Delta\omega'_{2l+3})^2 - \omega'^2 + \Gamma'^2_{2l+3} \right]^2 + 4\omega'^2\Gamma'^2_{2l+3}} \left\{ (1-\alpha)(2l+3 + \Delta\omega'_{2l+3} \right. \\
& + \omega' - i\Gamma'_{2l+3}) \left[(e^{-\beta E_l} - e^{-\beta E_{l+1}}) \left(\frac{l+1 + \Delta\omega'_{l+1} - \omega' - i\Gamma'_{l+1}}{(l+1 + \Delta\omega'_{l+1} - \omega')^2 + \Gamma'^2_{l+1}} \right. \right. \\
& + \left. \frac{l+1 + \Delta\omega'_{l+1} - i\Gamma'_{l+1}}{(l+1 + \Delta\omega'_{l+1})^2 + \Gamma'^2_{l+1}} \right) - (e^{-\beta E_{l+1}} - e^{-\beta E_{l+2}}) \\
& \times \left(\frac{(l+2 + \Delta\omega'_{l+2} - \omega' - i\Gamma'_{l+2})}{(l+2 + \Delta\omega'_{l+2} - \omega')^2 + \Gamma'^2_{l+2}} + \frac{l+2 + \Delta\omega'_{l+2} - i\Gamma'_{l+2}}{(l+2 + \Delta\omega'_{l+2})^2 + \Gamma'^2_{l+2}} \right) \Big] \\
& + (2l+3 + \Delta\omega'_{2l+3} - \omega' + i\Gamma'_{2l+3}) \left[(e^{-\beta E_l} - e^{-\beta E_{l+1}}) \right. \\
& \times \left(\frac{l+1 + \Delta\omega'_{l+1} + \omega' + i\Gamma'_{l+1}}{(l+1 + \Delta\omega'_{l+1} - \omega')^2 + \Gamma'^2_{l+1}} + \frac{l+1 + \Delta\omega'_{l+1} + i\Gamma'_{l+1}}{(l+1 + \Delta\omega'_{l+1})^2 + \Gamma'^2_{l+1}} \right) \\
& - (e^{-\beta E_{l+1}} - e^{-\beta E_{l+2}}) \left(\frac{l+2 + \Delta\omega'_{l+2} + \omega' + i\Gamma'_{l+2}}{(l+2 + \Delta\omega'_{l+2} - \omega')^2 + \Gamma'^2_{l+2}} \right. \\
& + \left. \frac{l+2 + \Delta\omega'_{l+2} + i\Gamma'_{l+2}}{(l+2 + \Delta\omega'_{l+2})^2 + \Gamma'^2_{l+2}} \right) \Big] (1-\alpha) \\
& \left. + \alpha(2l+3 + \Delta\omega'_{2l+3})(e^{-\beta E_l} - e^{-\beta E_{l+2}}) \right\} \Big], \tag{59}
\end{aligned}$$

$$\begin{aligned}
\Phi_2(\omega') &= \frac{(1-r)}{60} E^2 K_0 \sum_{l=0}^{\infty} \frac{l+1}{a} \left[\frac{2(1-\alpha)(\gamma'_l - 2i\omega')}{\gamma'^2_l + 4\omega'^2} \left\{ \frac{l}{2l+3} (e^{-\beta E_l} - e^{-\beta E_{l+1}}) \right. \right. \\
& \times \left(\frac{\Gamma'_{l+1} + i(l+1 + \Delta\omega'_{l+1} + \omega')}{(l+1 + \Delta\omega'_{l+1} + \omega')^2 + \Gamma'^2_{l+1}} - \frac{\Gamma'_{l+1} + i(l+1 + \Delta\omega'_{l+1} - \omega')}{(l+1 + \Delta\omega'_{l+1} - \omega')^2 + \Gamma'^2_{l+1}} \right) \\
& \left. - \frac{l}{2l-1} (e^{-\beta E_{l-1}} - e^{-\beta E_l}) \left[\frac{\Gamma'_l + i(l + \Delta\omega'_l + \omega')}{(l + \Delta\omega'_l + \omega')^2 + \Gamma'^2_l} - \right. \right.
\end{aligned}$$

$$\begin{aligned}
& -\frac{\Gamma'_l + i(l + \Delta\omega'_l - \omega')}{(l + \Delta\omega'_l - \omega')^2 + \Gamma'^2_l} \Bigg\} + \frac{3(l+2)}{2l+3} \\
& \times \left(\frac{2l+3 + \Delta\omega'_{2l+3})^2 - 4\omega'^2 - 4i\omega'\Gamma'_{2l+3}}{\left[(2l+3 + \Delta\omega'_{2l+3})^2 - 4\omega'^2 + \Gamma'^2_{2l+3}\right]^2 + 16\omega'^2\Gamma'^2_{2l+3}} \left\{ (2l+3 + \Delta\omega'_{2l+3} \right. \right. \\
& + 2\omega' - i\Gamma'_{2l+3}) \left((e^{-\beta E_l} - e^{-\beta E_{l+1}}) \frac{l+1 + \Delta\omega'_{l+1} - \omega' - i\Gamma'_{l+1}}{(l+1 + \Delta\omega'_{l+1} - \omega')^2 + \Gamma'^2_{l+1}} \right. \\
& - (e^{-\beta E_{l+1}} - e^{-\beta E_{l+2}}) \frac{(l+2 + \Delta\omega'_{l+2} + \omega' - i\Gamma'_{l+2})}{(l+2 + \Delta\omega'_{l+2} + \omega')^2 + \Gamma'^2_{l+2}} \Bigg) (1-\alpha) \\
& + (2l+3 + \Delta\omega'_{2l+3} - 2\omega' + i\Gamma'_{2l+3}) \left((e^{-\beta E_l} - e^{-\beta E_{l+1}}) \right. \\
& \times \frac{l+1 + \Delta\omega'_{l+1} + \omega' + i\Gamma'_{l+1}}{(l+1 + \Delta\omega'_{l+1} + \omega')^2 + \Gamma'^2_{l+1}} - (e^{-\beta E_{l+1}} - e^{-\beta E_{l+2}}) \\
& \times \frac{l+2 + \Delta\omega'_{l+2} + \omega' + i\Gamma'_{l+2}}{(l+2 + \Delta\omega'_{l+2} - \omega')^2 + \Gamma'^2_{l+2}} \Bigg) (1-\alpha) \\
& \left. \left. + \alpha(2l+3 + \Delta\omega'_{2l+3})(e^{-\beta E_l} - e^{-\beta E_{l+2}}) \right\} \right] \Bigg\}. \tag{60}
\end{aligned}$$

Relation (57) shows how frequency-time dependent Kerr optical function depends on field parameters like frequency and field strengths, on the molecular parameters like moment of inertia, dipole moment and polarisability, on the bath frictional parameter and on the temperature. Despite the fact that these results have been obtained in the limit of small coupling parameter B , they can still be used as first approximation to interpret experimental results on dense bath but at very low temperatures. We point out that, unlike earlier works on electrical susceptibility which have always considered that observed spectra are mainly accounted for by transitions involving $\Delta l = \pm 1$, these results on the Kerr optical effect predict, not only $\Delta l = \pm 1$ transitions, but also those with $\Delta l = \pm 2$.

3 Discussions

1) In constant temperature conditions, the response of a dielectric material to a low frequency external a.c. field is strong and is in phase with the latter for low frictional oscillator-bath and /or large inertia molecules ($\gamma = 0.5$ in Figure 1). From the energetic point of view, this in-phase aspect favours the external field effect on the rotator-bath system and thus increases the system's ability to capture energy from the surrounding. On the other hand, a totally different phenomenon is observed for high frequencies where a weak response sets in, tending to annihilate the field effect by appearing in anti-phase with the it (Figure 2). The first convergent of the classical susceptibility function corresponding to the Rocard result (the first approximation of the inertia effect) gives a maximum phase for a frequency of $\omega = \sqrt{2}\omega_{mean}$ whatever the γ value. At this frequency value collisions result to large energy exchanges of the order of $k_B T$. For higher γ values, there is a departure from this frequency value (see Figure 4).

2) The manifestation of quantum effects depends, not only on the coupling parameter ($B = \zeta/I$) but also on the temperature-inertia parameter $a = \hbar^2/(Ik_B T)$. This allows us to define a necessary condition for the domination of quantum effects. The inequality

$$s = B/\omega_{mean} = 1/\sqrt{\gamma} << \frac{1}{2} \left(\hbar^2 / Ik_B T \right)^{3/2} = a^{3/2}/2 \quad (61)$$

expresses this condition. For example, for $a = 0.05$, as the parameter s decreases from 0.025 through 0.010 to 0.001, we observe a passage from a continuous classical spectrum

through broadened lines to well defined discrete lines (Figure 5) meanwhile for $a = .5$ quantum effects are already present even for $s = .08$ (see Figure 6). This observation is also important for the Kerr spectra (see Figure 14).

3) The time variation of the classical Kerr electrical birefringence (KEB) is characterised by oscillations about $r - \omega$ dependent time constant values which decrease with increasing r and with increasing frequency. The 2ω -harmonic component is dominant for small r and large α values while the single ω one dominates for intermediate and higher r values, (see Figures 7-9). Physically, the doubling of period takes place by a process of progressive crushing of intermediate peak values in the KEB curve shape with increasing r . This period change is noticed by a set of pronounced transitions of non sinusoidal periodic regimes which takes place between two sinusoidal regime limits corresponding to the extreme r values ($E_a \ll E_c$ and $E_a \gg E_c$).

4) For constant bath parameters and for small and intermediate E_c/E_a ratio, the Kerr effect increases with increasing α , presenting small amplitude distortions that disappear to form secondary peaks as α grows, portraying the progressive appearance of the influence of the 2ω -harmonic component.

5) The Kerr spectral function for a.c.-d.c. coupling is

$$\begin{aligned} \tilde{\Phi}(\omega, \Omega) = & \left[2Re\Phi_0(\omega)\delta(\Omega) + \Phi_1(\omega)\delta(\Omega - \omega) + \Phi_1^*(\omega)\delta(\Omega + \omega) \right. \\ & \left. + \Phi_2(\omega)\delta(\Omega - 2\omega) + \Phi_2^*(\omega)\delta(\Omega + 2\omega) \right]. \end{aligned} \quad (62)$$

This shows that for an a.c. field of given frequency, all three terms cannot be measured simultaneously. The a.c.-d.c. field coupling on dielectrics, therefore, proves to be very useful as, depending on the harmonic component observed, we are able to predict the relative strengths of permanent dipole to induced dipole effects. The 2ω -component dominates for polarisable fluids (large α) while the ω -one dominates for less polarisable fluids (small α). More importantly, the observation of 2ω -harmonic component may also entail that the most probable rotational lines involve transitions like $l \rightarrow l \pm 2$ while the observation of ω harmonics concerns transitions $l \rightarrow l \pm 1$. This last point is very important when E_c and E_a are of the same order of magnitudes.

References

- [1] Navez P and Hounkonnou M N 1995 J. Phys. A **28**, 6345
- [2] Titantah J T and Hounkonnou M N 1997 J. Phys. A **30**,6327
- [3] Titantah J T and Hounkonnou M N 1997 J. Phys. A **30**,6347
- [4] Morita A 1978 J.Phys. D. **11** L9 4708
- [5] Morita A and Watanabe H 1979 J. Chem. Phys. **70** 4708
- [6] Matsumoto M, Watanabe H and Yoshioka K 1970 J. Phys. Chem. **74** 2182
- [7] Coffey W T 1990 J. Chem. Phys. **93** 724
- [8] Coffey W T 1990 J. Chem. Phys. **93** 171
- [9] Coffey W T 1991 J. Chem. Phys. **95** 2026
- [10] Mc Connel J 1980 *Rotational Brownian motion and Dielectric Theory* (New York: Academic)
- [11] Lindenberg k and West B J 1991 *The Non Equilibrium Statistical Mechanics of Open and Closed systems* (New York:VCH)
- [12] Morita A 1982 J. Chem. Phys. **76** 3198
- [13] Hounkonnou M N, Ronveaux A and Navez P 1994 J. Phys. A **27** 6635

- [14] Navez P and Hounkonnou M N, 1994 J. Phys. A **27** 6657
- [15] Hounkonnou M N, Ronveaux A and Hazoumé R P 1991 Physica **179** 569
- [16] Hounkonnou M N 1991 J. Chem. Soc. Faraday Trans. **87** 297
- [17] Hounkonnou M N and Ronveaux A 1992 Acta. Phys. **82** 425
- [18] Filippini J C 1972 Ph.D Thesis, Université de Grenoble France
- [19] Navez P 1995 Thèse de Doctorat ès Sciences, Université Catholique de Louvain
Belgium
- [20] Coffey W T and Paranjape B V 1978 Proc. R. Ir. Acad. **78** 17
- [21] Morita A and Watanabe H 1987 Phys. Rev. **35** 2690
- [22] Gross E P 1955 J. Chem. Phys. **23** 1415
- [23] Doi M and Edwards S F 1986 *The Theory of Polymer Dynamics*, Clarendon
Press Oxford
- [24] Morita A, Walker S and Calderwood J H 1976 J. Phys. D:App. Phys. **9** 2485
- [25] Stark B 1967 *Atomic and Molecular Constants from Microscopic Spectroscopy*
(Berlin: Springer-Verlag)

Figure Captions

Figure1 shows the plots, for $\nu = 0.15$, of: 1) $\cos \nu \tau$, and the reduced susceptibility $\chi_r(\nu, \tau)$ versus the dimensionless time $\tau = \omega_{mean} t$ for; 2) $\gamma = 0.05$, 3) $\gamma = 0.5$.

Figure2 shows the plots, for $\nu = 4.00$, of: 1) $\cos \nu \tau$ and the reduced susceptibility $\chi_r(\nu, \tau)$ versus the dimensionless time $\tau = \omega_{mean} t$ for; 2) $\gamma = 0.05$ and 3) $\gamma = 0.5$.

Figure3 shows the 3D plot, for $\gamma = 0.05$ and $r = 0$, of the reduced polarisation $\chi_r(\omega', \tau)$ versus the dimensionless time and frequency $\tau = Bt$ and $\omega' = \omega/B$, respectively.

Figure4 shows the 3D plot, for $\gamma = 0.05$, of $\tan(\alpha(\nu, \gamma))$ versus the dimensionless frequency $\nu = \omega/\omega_{mean}$ and γ (classical result).

Figure5 shows the plots of $\alpha(\omega')$ (in *rad*) versus the dimensionless frequency $\omega' = \omega/(\hbar/I)$ for $a = 0.05$: 1) $s = 0.025$, 2) $s = 0.01$ and 3) $s = 0.001$ (RWA).

Figure6 shows the plots of $\alpha(\omega')$ (in *rad*) versus the dimensionless frequency $\omega' = \omega/(\hbar/I)$ for $a = 0.5$: 1) $s = 0.25$, 2) $s = 0.08$ and 3) $s = 0.01$ (RWA).

Figure7 shows the plots of the classical Kerr function versus the dimensionless time $t' = Bt$ for $\omega/B = 1.0$, $\alpha = 0.1$: 1) $r = 0.95$; 2) $r = 0.5$ and 3) $r = 0.05$.

Figure8 shows the plots of the classical Kerr function versus the dimensionless time $t' = Bt$ for $\omega/B = 1.0$, $\alpha = 0.5$: 1) $r = 0.95$; 2) $r = 0.5$ and 3) $r = 0.05$.

Figure9 shows the plots of the classical Kerr function versus the dimensionless time $t' = Bt$ for $\omega/B = 1.0$, $\alpha = 0.9$: 1) $r = 0.95$; 2) $r = 0.5$ and 3) $r = 0.05$.

Figure10 shows the plots of the quantum Kerr function versus the dimensionless time $t' = t/(\hbar/I)$ for $\omega = 4\hbar/I$, $\alpha = 0.1$: 1) — $r = 0.95$: 2) --- $r = 0.5$ and 3) $r = 0.05$.

Figure11 shows the plots of the quantum Kerr function versus the dimensionless time $t' = t/(\hbar/I)$ for $\omega = 4\hbar/I$, $\alpha = 0.5$: 1) — $r = 0.95$: 2) --- $r = 0.5$ and 3).... $r = 0.05$.

Figure12 shows the plots of the quantum Kerr function versus the dimensionless time $t' = t/(\hbar/I)$ for $\omega = 4\hbar/I$, $\alpha = 0.9$: 1) — $r = 0.95$: 2) --- $r = 0.5$ and 3) $r = 0.05$.

Figure13 shows the plot of the real part of 1) --- the ω -harmonic component and 2) — the 2ω -harmonic component of the quantum Kerr function versus the dimensionless frequency $\omega/(\hbar/I)$ for $a = 0.05$, $s = 0.01$, $\alpha = 0.4$ and $r = 0.5$.

Figure14 shows the plot of the imaginary part of the ω -harmonic component of the quantum Kerr function versus the dimensionless frequency $\omega/(\hbar/I)$ for 1) — $a = 0.25$, $s = 0.10$, $\alpha = 0.4$, $r = 0.5$ and 2) --- $a = 0.05$, $s = 0.01$, $\alpha = 0.4$, $r = 0.5$.



























